PYROLYSIS OF SURFACE-IMMOBILIZED MODEL COMPOUNDS.
MECHANISTIC IMPLICATIONS FOR THE THERMAL CHEMISTRY OF COAL

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INTRODUCTION

The thermal reactivity of coal forms the basis of many processes devised for coal
utilization. Although much is known about the kinetics of coal pyrolysis,[1] a
detailed molecular level mechanistic understanding is hampered by the complex
chemical structure of coal. Organic compounds[2] and simple polymers[3] have been
employed beneficially as surrogates for coal in many studies of thermal and chemical
reactivity. However, the interpretive extrapolation of such model compound behavior
to coal should take into consideration some of the complexities inherent to coal.

Our research has been investigating the potential role that the cross-linked network
structure of coal may play in perturbing free-radical reactions associated with coal
thermolysis.[4-7] This may be particularly important in the thermal conversion of coal
at low temperatures, e.g., 350-400°C, where bonds begin to break but most of the
residual framework is retained. In order to assess the potential impact of restric-
ted transport on thermal reaction pathways, we have modeled the phenomenon experi-
mentally by studying organic model compounds that are covalently linked to an inert
silica surface. The experimental methodology and significant results from studies
of the thermolysis of surface-attached Ph(CH$_2$)$_n$Ph [n — 0-4] at 345-400°C will be
briefly surveyed. Initial results from studies of two-component surfaces will also
be presented that reveal the role of radical migration, via facile hydrogen
shuttling, in modifying the effects of diffusional constraints.

RESULTS AND DISCUSSION

Surface Attachment Methodology. The criteria for an appropriate support and
covalent link are substantial. Both must be stable in the temperature range of
interest (ca. 400°C). The support should have a moderately high surface area with
enough active sites for attaching significant quantities of the organic moieties of
interest. Any unreacted surface sites should not be catalytically active.
Furthermore, the position of surface attachment within the organic moiety should be
somewhat remote from the normal position of thermal reactivity. Finally, although
the covalent link should be thermally stable, there must be a facile method for
quantitative analysis of surface-bound reactants and products.

These criteria were met through the use of a high-purity, nonporous, amorphous fumed
silica as the support and a Si-O-C$_{aryl}$ linkage as the surface connection. The surface
attachment reaction is shown in Fig. 1, and the full experimental details are given
elsewhere.[4,5] In short, the standard procedure for preparation of saturation
coverage samples was to disperse an excess of the parent phenol onto predried silica
by evaporating benzene solvent from a slurry, to heat the resulting powder at 225°C
in a sealed, degassed tube to effect the surface reaction, and to evacuate the
product at 270°C to remove excess phenol and the water byproduct. Lower surface

coverages were prepared by limiting the amount of phenol relative to the surface hydroxyl population. As shown in Fig. 1, surface coverages were analyzed by a procedure that involves recovery of the phenol following digestion of the silica in aqueous base. Saturation surface coverages of 0.45-0.60 mmol organic/g of derivatized silica were obtained for a series of para-substituted α,ω-diphenylalkanes (Fig. 1). These coverages correspond to ca. 1.5 - 2.0 organic molecules/nm^2 surface area, or 35-45% derivatization of the ca. 4.5 surface OH/nm^2 available. An examination of these surface coverages with the use of model crystalline silica surfaces suggested a "liquid-like" monolayer with steric constraints prohibiting significantly higher coverages.[4]

Thermolysis Methodology.[4,5] Thermolyses were performed in sealed, evacuated (2 × 10^{-6} torr) T-shaped pyrex tubes in a configuration such that volatile products could be collected in a cold trap (77 K) as they formed. These products were analyzed by GC and GC-MS with the use of internal standards. In a separate procedure, surface-attached products were liberated as phenols following digestion of the silica in base, silylated to the corresponding trimethylsilyl ethers, and analyzed as above.

Thermolysis of Diarylalkanes. The surface-attached diphenylalkanes, $\bullet SiOC_6H_4(CH_2)_nC_6H_5$ [n = 0-4] (represented as ~~Ph(CH$_2$)$_n$Ph) were prepared, and their thermolysis behavior compared with that of the parent hydrocarbons in fluid phases. Major findings will now be briefly surveyed.

(1) Biphenyl and diphenylmethane are thermally stable at 400°C for many hours.[2] Heating ~~PhPh and ~~PhCH$_2$Ph at 400°C for 4 h showed only the evolution of 5-10% of the parent phenols into the cold trap. This minor reaction is analogous to the well-known dehydroxylation of silica itself, and the results indicated that this mode of surface attachment is robust enough to keep most of the organic moieties on the surface for several hours at 400°C. Most importantly, no new products, either volatile or surface-attached, were observed and, hence, the silica surface (e.g., residual surface hydroxyls) did not induce any new reaction pathways. This factor allows for the study of the influence of restricted diffusion on thermolysis reactions in the absence of other possible surface-induced perturbations.

(2) Studies of surface-immobilized bibenzyl[4] (~~PhCH$_2$CH$_2$Ph, or ~~BB) revealed that the unimolecular homolysis rate for the central C-C bond was independent of surface coverage and not affected by the mode of surface attachment. Analysis of the rate constants at 350-400°C gave activation parameters, E_a = 62.9 ± 1.8 kcal/mol and A = 10$^{(15.3 \pm 0.6)}$s^{-1}, that are comparable to fluid phase values. A comparison of the homolysis rate constants for gaseous,[8,9] liquid (tetralin),[8,10] and surface attached bibenzyl at 375°C are thus 2.2 × 10^{-6}, 1.1 × 10^{-6}, and 1.2 × 10^{-6} s^{-1}, respectively. Although more examples are needed, these results give added confidence to the extrapolation of bond homolysis rates for ArCH$_2$CH$_2$Ar' model compounds to comparable dimethylene bridges in coal.

Studies of ~~BB also showed that dramatically altered product distributions can result from diffusional constraints. This is illustrated in Fig. 2, which compares the major product selectivities for ~~BB at high surface coverage (0.465 mmol/g) with that of liquid BB at comparable low conversions (ca. 1.5%). The major finding was that restricted diffusion enhances the rates of free-radical chain processes on the surface that result in rearrangement [to ~~PhCH(Ph)CH$_3$] and cyclization [to ~~dihydrophenanthrene and ~~phenanthrene] of ~~BB. The kinetic chain length for rearrangement was enhanced some 30-fold compared to liquid-phase BB. Note also that some of the hydrogen eliminated (or transferred) during the cyclization-dehydrogenation process induced significant amounts of cleavage of the much stronger C$_{ar}$-C$_{al}$ bonds. The enhanced rates of chain rearrangement and cyclization (which cycle through ~~PhCH•CH$_2$Ph and ~~PhCH$_2$CH•Ph) were closely coupled to a dramatically

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decreased rate for radical-radical coupling on the surface, which would likely serve as an important chain termination step. This is evidenced by the disappearance of tetraphenylbutanes as thermolysis products on the surface, whereas they were major products in the liquid BB reaction (Fig. 2). The rearrangement and cyclization reactions provide retrogressive pathways toward more refractory materials during coal pyrolysis. In coal liquefaction, good hydrogen donor solvents (DH) may play an additional role of chain inhibitor by transferring radical centers from immobilized ArCH·CH$_2$Ar' to D·, which are free to diffuse and terminate chains.

(3) Earlier studies of fluid phase 1,3-diphenylpropane (DPP)[11,12] were important in establishing that C$_3$-links between aromatic and heteroaromatic clusters in coal could decay at significant rates at 350-400°C as a result of a free-radical chain decomposition pathway, even though the weakest C-C bond in DPP has a bond strength of ca. 74 kcal/mol. Our recent studies of surface-attached DPP suggested that these types of linkages can also decay efficiently in this temperature regime even under conditions of restricted diffusion.[5] --DPP thermally cracked to give two sets of products (the two ends of the molecule are dissimilar) as shown below.

--Ph(CH$_2$)$_3$Ph → --PhCH$_3$ + PhCH=CH$_2$ and   --PhCH=CH$_2$ + PhCH$_3$
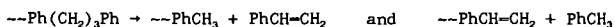
The chain propagation steps are shown in Fig. 3 where the parentheses in the hydrogen transfer step indicate that both vapor-phase and surface-attached species undergo the reaction. The overall rate of decomposition of --DPP at high coverages (7-9 %/h at 375°C, 0.57-0.59 mmol/g) is comparable to that of liquid DPP. However, the rate was found to be even more sensitive to surface coverage than the rate of fluid-phase DPP thermolysis is to concentration with the rate decreasing to 0.26 %/h at the lowest coverage studied (0.102 mmol/g). The restricted mobility also induced regioselectivity in the thermolysis of --DPP. The regioselectivity is determined by the relative concentration of the two benzylic radicals, [--PhCH$_2$CH$_2$CH·Ph]/ [--PhCH·CH$_2$CH$_2$Ph], and can be experimentally monitored by the PhCH=CH$_2$/PhCH$_3$ yield ratio, S. In related fluid phase studies of Me$_3$SiOPh(CH$_2$)$_3$Ph[13], a slight inherent substituent effect, S = 0.91, was observed, indicating a slight stabilization of the benzylic radical para to the siloxy substituent. The corresponding inherent selectivity for --DPP at high surface coverages from data extrapolated to zero --DPP conversion was ca. 0.95. However, the selectivity gradually increased (S > 1.0) with increasing conversion and decreasing initial surface coverage. For example, at a coverage of 0.10 mmol/g and a --DPP conversion of 2.8%, we found S = 1.30. It appears that as --DPP molecules become increasingly distant from hydrogen abstracting radicals on the surface, geometrical constraints induced by the restricted mobility begin to favor hydrogen abstraction at the benzylic methylene site farthest from the surface as illustrated in Fig. 4. Hence, the efficiency and regioselectivity in the thermal cleavage of such linkages in coal will likely depend on their immediate environment and on the presence or absence of mobile radical sources.
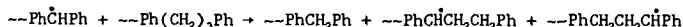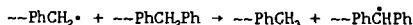
(4) Studies of surface-attached 1,4-diphenylbutane (--DPB) are now being pursued to further explore the regioselectivity of hydrogen transfer induced by restricted mobility.[8] As shown in Fig. 5, --DPB decays readily at 400°C to four sets of products via a radical chain process analogous to --DPP, which cycles through radicals at the four distinct positions labeled in the polymethylene chain. The selectivity for the products derived from the two benzylic carbon radical sites, 4/1 (as measured by PhCH=CH$_2$/PhCH$_2$CH$_3$ yield ratio) increases with increasing conversion and decreasing surface coverage as did the analogous selectivity for --DPP. However, --DPB also shows substantial cracking occurring through nonbenzylic radical counterparts. Clearly at high surface coverage all four cracking pathways are competitive (Fig. 5). Our accumulating evidence indicates that rapid hydrogen transfer reactions with parent --DPB allow interconversion of benzylic and nonbenzylic radical sites. [The nonbenzylic radicals actually have faster rates for β-

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scission, and an analogous proposal for radical interconversion has been made for the case of fluid phase DPB.[11]]

   e.g.,   ~~1-DPB• + ~~DPB ⇌ ~~DPB + ~~2-DPB•
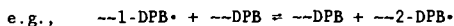
This concept of rapid hydrogen transfer reactions occurring on the surface is supported by studies of ~~DPB at lower surface coverages, which hinder the radical interconversion process. For example, decreasing the surface coverage from 0.541 to 0.054 mmol/g substantially increases the 1/2 selectivity (measured from $PhCH_2CH_3$/ $PhCH_3$ ratio) from 1.18 to 2.01. Additional supporting evidence is obtained from current studies of two-component surfaces described below.

(5) Two-component surfaces containing ~~DPP with co-attached aromatics (shown in Fig. 6) were prepared having coverages for ~~DPP and the co-attached aromatic in the ranges of 0.10-0.17 mmol/g and 0.37-0.51 mmol/g, respectively. The results showed that the rate and regioselectivity of ~~DPP thermolysis is dependent on the structure of neighboring molecules on the surface. While the presence of ~~BP or ~~NAP has only small effects on the ~~DPP thermolysis compared with ~~DPP alone at similar surface coverages, the presence of ~~DPM dramatically alters both the rate and regioselectivity of the ~~DPP reaction. For single component samples of ~~DPP with coverages of 0.566 and 0.142 mmol/g, the ~~DPP conversion rates at 375°C were 6.6 and 0.39 %/h respectively. On the other hand a material containing ~~DPP/~~DPM (0.133/0.368 mmol/g) gives a ~~DPP thermolysis rate of 5.8 %/h, the same as high coverages of ~~DPP within our experimental error. Moreover, values for the regioselectivity, S, for this two component surface are in the range of 0.95 (similar to high coverages of ~~DPP at low conversions) with little dependence on ~~DPP conversion. These results along with supporting evidence from related studies using the deuterated analog, ~~DPM-d_2, strongly suggest that facile hydrogen transfer reactions involving ~~DPM are allowing radical centers to "migrate" on the surface, e.g.:

  ~~PhCH₂• + ~~PhCH₂Ph → ~~PhCH₃ + ~~PhĊHPh

  ~~PhĊHPh + ~~Ph(CH₂)₃Ph → ~~PhCH₂Ph + ~~PhĊHCH₂CH₂Ph + ~~PhCH₂CH₂ĊHPh

The result of such a process is to effectively decrease the distance between a ~~DPP molecule and a radical center on the surface. Not only does this enhance the rate at which ~~DPP reacts (compared with ~~DPP alone at a similar low surface coverage), but it also eliminates the distance-dependent conformational constraints on the hydrogen abstraction reactions from ~~DPP that lead to the regioselectivity in product formation. We have now observed similar effects in studies of ~~DPB/~~DPM (0.060/0.465 mmol/g), in which the 1/2 selectivity (1.17) is again substantially quenched and more characteristic of high surface coverages of ~~DPB (see above). The observation of facile hydrogen shuttling on the surface has important implications for coal pyrolysis. It provides evidence for a chemical means for "mobilizing" radical centers in a diffusionally constrained environment, which could have a substantial impact on the efficiency with which similar structural features would be cleaved in coal.

   SUMMARY

The technique of model compound immobilization by covalent surface attachment is providing valuable insights into the role of restricted diffusion on thermal reaction pathways, which could be of relevance to coal and other macromolecular

systems. This methodology should be readily extended to the study of other chemical
systems of interest, and to probing other mechanistic aspects of the thermal
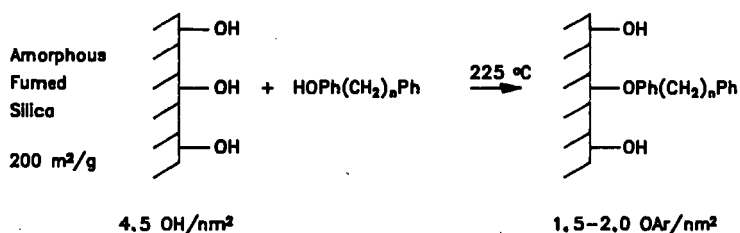chemistry of coal.

ACKNOWLEDGEMENTS

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Figure 1. Surface Attachment Reaction

Amorphous
Fumed
Silica

200 m²/g

—OH

—OH + HOPh(CH₂)ₙPh

—OH

4.5 OH/nm²

$\xrightarrow{225\ °C}$

—OH

—OPh(CH₂)ₙPh

—OH

1.5–2.0 OAr/nm²

Surface Coverage Analysis:

$\geq$SiOAr $\xrightarrow{\begin{array}{c}1)\ OH^-/H_2O,\ 25\ °C\\ \\ 2)\ H_3O^+/CH_2Cl_2\end{array}}$ ArOH
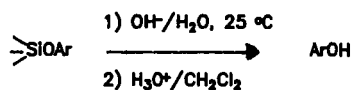
Figure 2. Effect of surface-immobilization on bibenzyl thermolysis

[Surface-immobilized]

$$\text{wwPhCH}_2\text{CH}_2\text{Ph} \longrightarrow \text{wPh}\overset{\overset{\text{Ph}}{|}}{\text{C}}\text{HCH}_3 + \text{wPhCH}_3 + \text{PhCH}_3 + \text{wPhenH}_2 + \text{wPhen}$$

(65%)   (7%)   (6%)   (6%)   (2%)

+ wwPhCH=CHPh + wPhC₂H₅ + PhH + wPhH + PhC₂H₅

(4%)   (2%)   (2%)   (2%)   (2%)

[Liquid]

PhCH₂CH₂Ph $\longrightarrow$ PhCH₃ + (PhCH₂CHPh$\rightarrow$)₂ + Ph₂CHCH₃ + PhCH=CHPh

(56%)   222(23%)   (10%)   (9%)
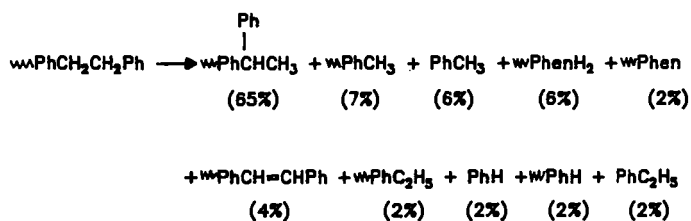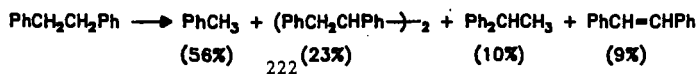
Figure 3. Radical chain propagation steps for ᵂᵂDPP

ᵂᵂ Ph(CH₂)₃Ph + (ᵂᵂ)PhCH₂ •

ᴬᴬᴬ PhĊHCH₂CH₂Ph + (ᵂᵂ)PhCH₃

ᴬᴬᴬ PhCH₂CH₂ĊHPh + (ᵂᵂ)PhCH₃

ᴬᴬᴬ PhĊHCH₂CH₂Ph ⟶ ᵂᵂ PhCH=CH₂ + PhCH₂ •

ᴬᴬᴬ PhCH₂CH₂ĊHPh ⟶ ᵂᵂ PhCH₂• + PhCH=CH₂

Figure 4. Regiospecific Hydrogen Transfer

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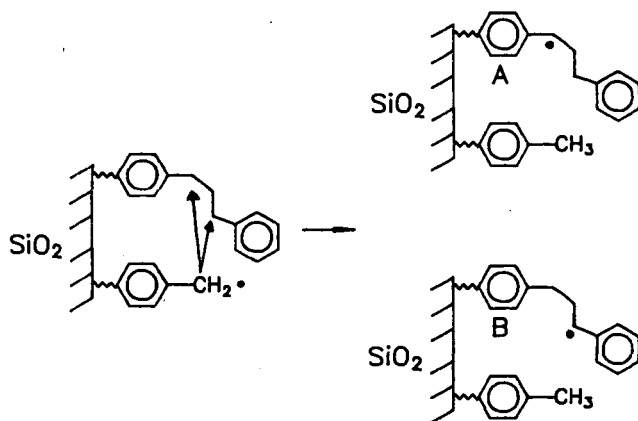
Figure 5. Thermolysis of ∿Ph(CH$_2$)$_4$Ph at 400 °C ;

Selectivity: (1) 1.18 (2) 1.00 (3) 1.09 (4) 1.22

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                                    1
                                   ┌──► ∿∿ PhCH=CH₂    +    PhCH₂CH₃
                                   │
                                    2
        1  2  3  4                 ├──► ∿∿ PhCH₂CH=CH₂   +   PhCH₃
   ∿∿ PhCH₂CH₂CH₂CH₂Ph  ──────────┤
                                    3
        (0.54 mmol/g)              ├──► ∿∿ PhCH₃    +    PhCH₂CH=CH₂
                                   │
     (2.4% conv in 10 min)         4
                                   └──► ∿∿ PhCH₂CH₃    +    PhCH=CH₂
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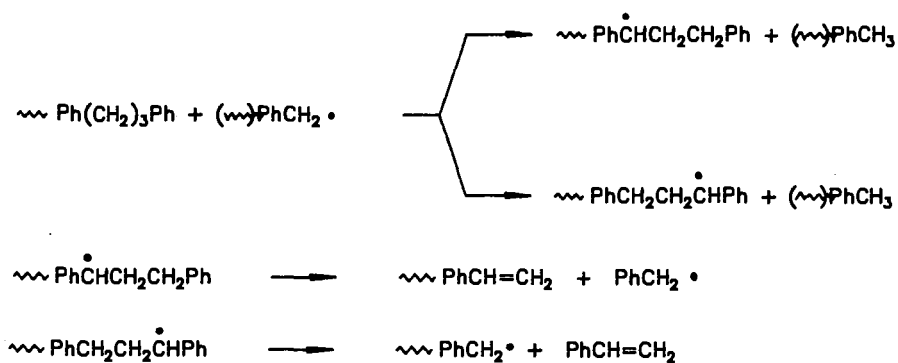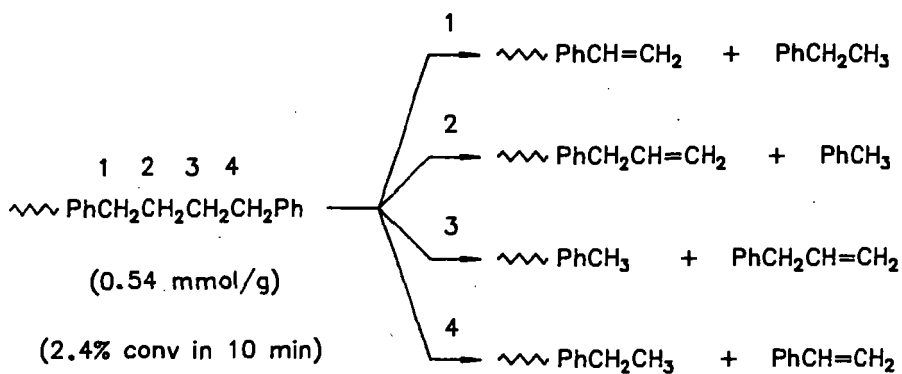
Figure 6. Two-component surfaces studied

∿∿DPP / ∿∿BP   ∿∿DPP / ∿∿NAP   ∿∿DPP / ∿∿DPM

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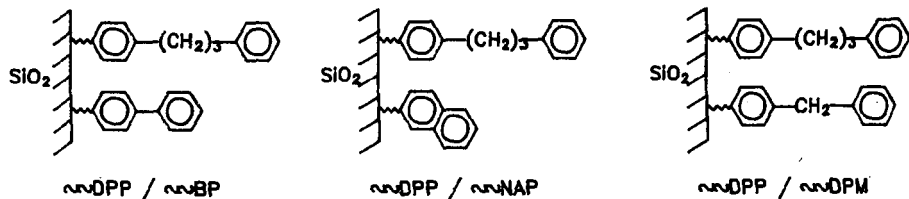
REACTIVE INTERMEDIATES IN COAL LIQUEFACTION

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KEYWORDS: Reactive intermediates, radicals, cations.

INTRODUCTION: Investigations into the mechanisms of coal lique-
faction are hampered by the difficulty in obtaining information
at the molecular level. The chemical structure of the starting
coal is poorly defined and the products can be only partially
identified. Traditionally, mechanisms have been discussed in
terms of the yields of phenomenologically defined fractions such
as oils (pentane soluble product) and asphaltenes (pentane
insoluble, benzene soluble products). While these pseudo-compo-
nents have practical importance, their relation to molecular
processes is unsure. An approach to understanding the physical
organic chemistry of liquefaction using a method to monitor the
presence of reactive intermediates has shown promise (1,2). This
approach makes use of probe compounds to measure the prevalence
of selected reactive intermediates. A further extension of this
work is described here.

Compounds which can be shown to give distinct products upon
reaction with different reactive intermediates are selected to
probe for the presence of those intermediates. For example, 1,5-
dimethylnaphthalene undergoes de-methylation in the presence of
hydrogen atoms, hydrogenates to the methyltetralins in the pres-
ence of catalytic hydrogenation sties, and undergoes rearrange-
ment of the methyl groups to give the 1,6- and 2,6-dimethyl
isomers in the presence of acids or acidic catalyst sites (2).
Equally important is the fact that little or no product cross-
over occurs. That is, little isomerization is found in the
presence of a good radical initiator and little or no de-methyl-
ation is found in the presence of an acid catalyst. Thus, the
occurrence of isomerized methylnaphthalenes among the reaction
products is indicative of the presence of cationic pathways, and
the occurrence of methylnaphthalenes is indicative of the pres-
ence of hydrogen atoms and/or hydrogen atom donors.

The question of whether or not structures resembling dimethyl-
naphthalene are present in coal is immaterial. The purpose of
the probe compounds is to detect the presence of reactive inter-
mediates, not to mimic a bond thought to be present in the coal.
This differentiates the probes from the model compounds often
seen in the literature. Thus, while 1,6-dimethylnaphthalene may

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bear some resemblance to a coal model compound, it is only one example of compounds which can be used as mechanistic probes. Other compounds previously used as probes include 1,3-dimethyl-naphthalene(1), cis-decalin(1,2), and a tricyclodecane(2). The tricyclodecane is a good example of a probe with no coal-like bonds. The fact that little if any evidence exists for tricyclic compounds in coal has no effect on its ability to distinguish the presence of reactive free radicals.

EXPERIMENTAL: The compounds used as probes were obtained from Aldrich and contained less than 1% impurities as determined by GC. They were used without further purification. The commercial silica alumina (D980-13) was obtained from W.R. Grace (grade 980-13, 13% alumina) as an extrudate. The friable solid was ground with a mortar and pestle, and oven-dried at 150°C over-night. The molybdenum trisulfide was prepared from ammonium tetrathiomolybdate by precipitation from an aqueous solution using formic acid.(3) This procedure is best carried out in a hood because of the hydrogen sulfide formed. The ammonium tetra-thiomolybdate obtained from Aldrich was used without further purification.

All reactions were performed using 40-mL 316-stainless steel reactors. The 8-gram reaction mixtures contained the probe (200 mg); a silica-alumina (10 mg), molybdenum trisulfide (10 mg), bibenzyl (2.0 g), or coal (up to 1.5 g Ill. No.6) additive; and n-octacosane solvent. The reactors were pressurized to 1200 psig with hydrogen, heated to 425°C within 5-6 minutes by plunging them into a preheated fluidized sand bath, and shaken at temper-ature for 60 minutes. The products were washed from the cooled reactor using inhibitor-free tetrahydrofuran (Aldrich 27,038-5). The reaction mixtures were analyzed by GC-MSD using a Hewlett-Packard 5890 GC with a model 5970B MSD operated in the total ion mode. The GC quantitation was performed using internal standards with an estimated error of ±3%. The analysis of the coal has been reported.(1)

RESULTS AND DISCUSSION: One of our first probe studies of lique-faction mechanisms used 1,3-dimethylnaphthalene to demonstrate that the selectivity of the hydrogen atom mediated hydrocracking reaction is increased in the presence of coal.(1) This probe produces 1-methylnaphthalene upon hydrogen atom attack at the 3-position and 2-methylnaphthalene upon attack at the 1-position. The effect of added coal is shown in Figure 1 where the percent yields of the mono-methylnaphthalenes are plotted as a function of the amount of added Illinois No.6 coal. Separate experiments without added probe showed that less than 15% of the increase was due to coal derived material co-eluting with the methylnaph-thalenes. The increase in the total yield of methylnaphthalenes (top line) with added coal indicates that the net effect of the added coal is to enhance the amount of hydrogen atom transfer to the probe. The ability of the coal to produce hydrogen atoms or

hydrogen atom donors is greater than its ability to consume them. This additional activity results in the production of mostly 2-methylnaphthalene. As can be seen from the plots of the individual isomers (lower lines), the production of 1-methyl-naphthalene remained relatively constant. Thus, the addition of the coal affects not only the prevalence of the hydrogen atom reactions but also the selectivity with which they occur. This change in selectivity has been associated with the nature of the hydrogen atom donor.(1)

More recently, our efforts have been devoted to exploring the changes in mechanism associated with the addition of liquefac-tion catalysts.(2) These systems are expected to be even more challenging than the thermal systems because cationic processes may become important in the presence of added catalysts. Cation-ic processes generally are not considered to be important in the thermal reactions of coal. Indeed, our previous work showed no evidence of cationic activity strong enough to result in the rearrangement of the 1,3-dimethylnaphthalene.(1) Added liquefac-tion catalysts may contain acid sites associated with the cata-lyst supports or with the metal sulfides themselves. Mild cat-ionic character has been associated with an unsupported molyb-denum sulfide hydrogenation catalyst.(4) Mechanistic probes should provide evidence to substantiate or refute the importance of cationic processes during catalytic liquefaction.

A probe chosen to distinguish among several mechanisms was 1-ethylnaphthalene. Products that may be obtained from this probe by various pathways are shown in Figure 2. That the products can be related to the presence of distinguishable reactive inter-mediates was established by the data given in Table I. In the absence of any additive, a small amount of hydrogenation to the ethyltetralins (4%) and de-alkylation to naphthalene (6%) occur but the majority of the recovered material is un-reacted 1-ethylnaphthalene. The effect of the addition of the known radical initiator, bibenzyl, is to increase the naphthalene yield. Since the reaction is carried out under hydrogen, the increased de-alkylation is attributed to the hydrogen atom mech-anism proposed by Vernon.(5) However, the addition of the free radical source affected neither the yield of rearranged nor the yield of hydrogenated products. In contrast, the addition of the commercial silica alumina catalyst, D980-13, caused a dramatic increase in the extent of rearrangement. While the amount of ethylnaphthalene recovered is the same as in the blank, 62%, the major portion of it has been isomerized to the 2-isomer. Signif-icantly, no increase in the extent of de-alkylation nor in the extent of hydrogenation was observed. Thus, the isomerization to form the 2-ethylnaphthalene can be used as an indication of the cationic activity since this product is formed in the presence of the silica alumina catalyst but not in the presence of the radi-cal initiator. Similarly, the formation of naphthalene can be used as an indication of the extent of hydrogen atom activity since it is formed in the presence of the bibenzyl initiator but not in the presence of the silica alumina catalyst.

The above comparisons serve as the basis for the interpretation of the results obtained in the presence of other catalysts. Our initial investigations have focused on molybdenum trisulfide. This material is used as a precursor to the molybdenum disulfide which is formed under the reaction conditions.(6) The disulfide is thought to be the active form of the catalyst. Molybdenum trisulfide has been shown to be an effective liquefaction catalyst precursor under typical reaction conditions.(7) The fourth column of data in Table I shows the results obtained for this molybdenum sulfide catalyst. The appearance of rearranged ethylnaphthalene among the reaction products indicates that the molybdenum sulfide has some cationic character. Although the absolute amount of 2-ethylnaphthalene is only 6%, it accounts for over 25% of the additional products formed in the presence of the sulfide and is well above that formed in the absence of any additive or in the presence of bibenzyl. The yield of naphthalene is the same as was found in the blank; the molybdenum sulfide does not appear to enhance nor diminish this hydrogen atom mediated reaction. The main effect of the molybdenum trisulfide is to enhance the extent of hydrogenation as evidenced by the increased yield of ethyltetralins. The hydrogenation activity displayed by the trisulfide may involve acid sites or proton transfer to the substrate, but the hydrogenation probably does not proceed via a hydrogen atom transfer to produce a free hydronaphthyl radical.

Whether there is an intimate link between the observed hydrogenation and cationic activities or whether they are simply parallel, unrelated reactions cannot be determined from the above data. It has been proposed that anion vacancies are necessary for the binding of the substrate prior to hydrogenation.(8) Also, the chemisorbed hydrogen on the catalyst surface has been described as acidic hydrogen.(9,10) To further investigate the correlation of cationic behavior with hydrogenation behavior, the effect of added quinoline on the extent of these reactions was determined. These data are shown in Figure 3 where the yields of these two classes of products are plotted against the amount of added quinoline expressed as its molar ratio to molybdenum. The two graphs are remarkably similar. Added quinoline has little effect up to a ratio of about 1. Higher levels of addition cause decreased yields of both rearranged product and hydrogenation products. Thus, it appears that the acidic character of the molybdenum sulfide and its hydrogenation ability are correlated. Whether this correlation is causative cannot be determined from these data, but the results are very suggestive. The amount of quinoline needed to affect the catalyst activity was high. It was anticipated that inhibition of activity would occur at much lower levels of base because the active sites are on the catalyst surface only. Since stoichiometric amounts of base were needed to inhibit the hydrogenation activity, a simple interpretation based on non-competitive poisoning of the surface sites is insufficient to explain the observed inhibition.

CONCLUSIONS: The use of probe compounds in the study of coal liquefaction provides mechanistic details unavailable through the more traditional approaches. The approach has been applied to the study of the thermal liquefaction of coal and to liquefaction catalysts in the absence of coal. The current application to molybdenum sulfide catalysis has shown the precursor, molybdenum trisulfide, to be inactive in promoting free radical reactions. The dominate hydrogenation activity of the catalyst appears to be closely associated with its mild acidic character. Studies extending the technique to other catalysts and to catalytic coal liquefaction are currently under way.

DISCLAIMER: Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the U.S. Department of Energy.

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TABLE I. Product Distribution from 1-Ethylnaphthalene (mole %).

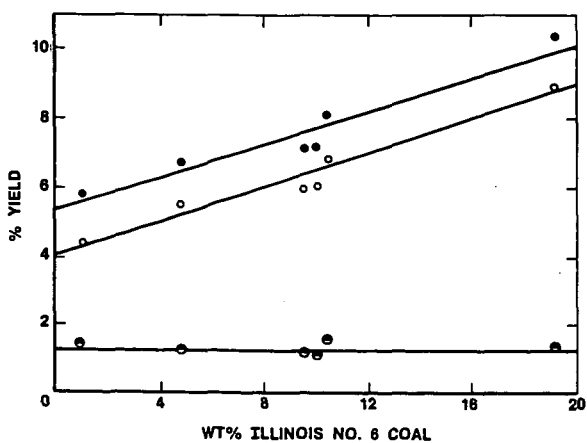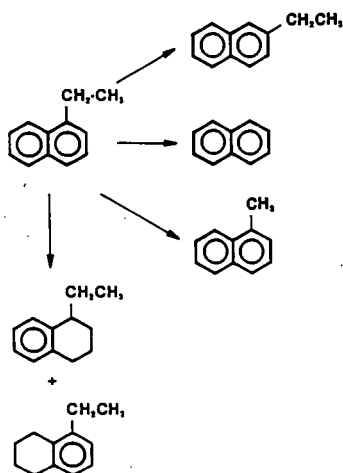|	Additive			
	None	Bibenzyl	D980-13	MoS$_3$
1-Ethylnaphthalene	62%	69%	19%	64%
2-Ethylnaphthalene	1	1	43	6
Naphthalene	6	19	3	7
Ethyltetralins	4	3	1	17
1- & 2-Methylnaph.	1	4	1	1
RECOVERY	73%	96%	67%	95%

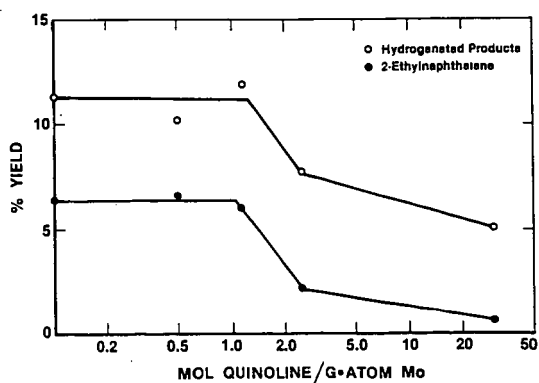
FIGURE 1.

NO./19.371

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FIGURE 2.

FIGURE 3.

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PHYSICAL ORGANIC CHEMISTRY OF COAL LIQUEFACTION

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The direct conversion of coal to liquid fuels is a complex chemical and physical process. The challenge of developing an understanding of the molecular details of this process has provided physical organic chemists great opportunities to ply their trade. Although dramatic breakthroughs may be lacking, progress has been made bit-by-bit. Along the way, a fascinating chemistry has been revealed. The extreme reaction conditions required for effective liquefaction have added an extra degree of interest to the development of this field.

Direct liquefaction is most often practiced by the addition of hydrogen to coal in some manner. The hydrogen content of the products is thus greater than that of the feedstocks. Accordingly, one of the central interests of our effort over the years has been the chemistry of hydrogen transfer reactions. Some form of hydrogen transfer is involved in nearly every chemical mechanism of importance to liquefaction (1). To fully understand the hydrogen transfer chemistry is to understand a large portion of the whole of liquefaction chemistry.

Many basic types of hydrogen transfer reactions may take place under liquefaction conditions. In the face of this inherently complex system, numerous experimental techniques for deriving information about these reactions have been developed. Some approaches have aimed at obtaining fundamental information about individual reactions, often by use of pure compounds under liquefaction conditions. Other approaches have focused on tracking the transfer reactions in liquefaction systems containing coal, with interest in finding what functional groups are the major players. Still another approach is a hybrid, using the addition of individual compounds to coal liquefaction feed slurries to gain information on the reaction environment under actual liquefaction conditions.

Past work in this laboratory on hydrogen transfer chemistry focused on the rates of transfer from individual compounds thought to be representative of constituents of liquefaction solvents to a simple, resonance-stabilized free radical (2,3). For this purpose, the benzyl radical was chosen as the hydrogen ac... ;:or because it represents, in general, the type and activity of radicals that are expected to form in coal under thermolytic conditions. One of the earliest mechanistic interpretations of liquefaction, in terms of simple molecular reaction steps, postulated that thermal scission of the weaker bonds in coal produced free radicals. The capping of these reactive intermediates by hydrogen transfer from hydroaromatic

compounds in the solvent before they could recombine led to liquid products (4). Although this simple, early view has since been shown to be incomplete, it nonetheless accounted for several important observations such as the correlation of the degree of coal conversion with the degree of conversion of hydroaromatic compounds in the liquefaction solvent to aromatic compounds. It also contained the important concept that the distribution of liquefaction products between extractable materials and residues results from the outcome of competitive reactions. Thus, the relative rates of hydrogen transfer versus the rates for condensation reactions are of importance because they relate directly to product distribution and product quality. If the rates of transfer from different hydrogen donors vary according to their structure, then it is of value to know the relative rate constants for transfer as well as the total concentration of donable hydrogen.

A series of competition experiments was performed to establish a scale of relative hydrogen transfer rate constants (2,3). The benzyl radical was provided by the thermolysis of easily decomposed compounds, dibenzylmercury (3) or dibenzyldiazene (2), at modest temperatures, typically 170^0C. Competition for the radicals was established between triphenylsilane-D and one of a number of donors, such as tetralin or dihydroanthracene. The relative rate constants were derived from the amount of deuterium incorporated into toluene, the product derived from the transfer of hydrogen or deuterium to a benzyl radical. These data illustrate that the rate constants vary considerably. For example, the value for transfer from dihydroanthracene is about a factor of 30 greater than that from tetralin. In perspective, such relative values bear on several aspects of liquefaction mechanisms. First, in regard to liquefaction yields, the type of donable hydrogen is important, not just the total amount of donable hydrogen. Second, the predominant free radicals generated in the liquefaction system should result from abstraction of hydrogen from the sites of greatest relative reactivity. The structures to be exhausted first among the different donors of a complex mixture may then be predicted. Also, the hydroaromatic radical species resulting from competitive abstraction reactions may be anticipated. The nature of these radicals takes on importance in light of the recent work showing that hydroaromatic radicals may serve to induce cleavage of strong bonds by donation of hydrogen atoms (5). As shown in the reference, hydrogen transfer from 9-hydroanthracenyl radical to an alkylaromatic compound yields anthracene and the cleavage products, which are the corresponding aromatic compound and the alkyl radical derived from the alkylaromatic. Finally, although the relative rate constant for hydrogen abstraction from each of the various donors is an important factor, it should be noted that this one parameter is hardly an infallible guide to success in liquefaction. It is only one part of the complicated mechanism, and simple attempts to correlate liquefaction yields with just one parameter most often fail.

A sidelight to these investigations arose from the observations that the kinetic deuterium isotope effects for transfer were unexpectedly large (6). A value for k_H/k_D as large as 13.0 was observed at 110^0C for the transfer from tetralin to benzyl radical.

Detailed investigations of this curiously large effect led to the conclusion that a tunneling mechanism must come into play for hydrogen transfer between these benzylic reaction partners (6). This provides another fascinating example of the complexity of the chemistry that takes place during liquefaction.

The second means to investigate hydrogen transfer reactions uses quite a different approach. In this approach, the important thing is the amount of hydrogen used or produced in various general types of organic reactions during liquefaction. For the purposes of discussion and accounting, the utilization of hydrogen may be broken down into four general types of reaction: production of light hydrocarbon gases; removal of heteroatoms by formation of water, H_2S, or ammonia; reduction of aromatic carbon; and the breaking of bonds, either those in the coal matrix or those in the liquefaction solvent (7). The amount of hydrogen used in each of these general processes may be determined by a combination of elemental analyses, mass balance data, and NMR determinations of aromaticities. The appropriate differences are then taken between the values for the starting materials and the values for the total organic products, including gases, methylene chloride extracts, and the extraction residue. From the results, some important general trends emerge. The aromaticity of the products tends to increase with liquefaction temperature. An overall gain in aromatic carbon was observed when temperatures over 400°C were reached (7). This trend was found even at 2000 psig hydrogen whether or not a catalyst was present (8). Thus, the higher temperatures normally used in the common liquefaction processes tend to work against the goal of coal hydrogenation.

Study of the effect of molybdenum catalysts used under low severity conditions also led to interesting observations. From the differing patterns of hydrogen utilization in catalytic and non-catalytic systems, one function of a dispersed catalyst derived from ammonium molybdate was to lessen the net number of retrogressive or condensation reactions (8). Thus, in comparing liquefaction experiments at 450°C, the number of hydrogens used per 100 carbon atoms for matrix bond breaking increased on addition of catalyst, but the number released from dehydrogenation of aromatic carbons was nearly the same. By following these changes as a function of reaction time, a picture of the sequence of utilization patterns could be developed (9). The results of this work indicated that condensation reactions were prominent during the first 10 minutes of reaction, after which cleavage reactions began to predominate. On the other hand, conversion to THF soluble material increased steadily throughout this same period of time. Obviously, a one-to-one correspondence of net bond cleavage and conversion does not exist. This work reveals that liquefaction kinetics appear differently according to whether conversion or hydrogen utilization is taken under study.

The critical nature of the first few minutes of a liquefaction reaction has recently become evident again through observations of the changes in total pressure within the liquefaction reactor with time. The total pressure was monitored during the course of the liquefaction reaction by mounting pressure transducers on microautoclaves. The data in Figure 1 for an Illinois No. 6 coal

show that the change in total pressure in the reactor is a function of the amount of ammonium tetrathiomolybdate added. The thiomolybdate serves as a precursor that is reduced in situ to form a molybdenum sulfide catalyst. If no catalyst precursor is added at all (data not shown), the increase in total pressure during the first 10 to 20 minutes of reaction is even more prominent than for the smallest addition of catalyst. At still larger additions, the pressure increase is not observed at all. Gas analysis of the products indicates that the major species in the gas phase after hydrogen is CO_2. The amount of CO_2 formed is not much different whether or not catalyst is present. Thus, it appears that at the higher concentrations, the catalyst acts in some way to induce the transfer of gas phase hydrogen in an amount that nearly balances the CO_2 evolved during the initial liquefaction. At the comparatively low temperature used for liquefaction here, it was also possible to see an increase in the conversion of coal to THF soluble material as a consequence of catalyst addition. Separate techniques thus point to the early time period of the liquefaction reaction as being especially critical to the pattern of hydrogen utilization. Clearly, any particular pattern is not universal, because many variables govern the kinetics of the four basic types of reaction. However, the hydrogen utilization methodology provides a means to monitor net changes in the patterns of the hydrogen transfer reactions as the process parameters are manipulated.

A third general methodology employed in our laboratories has been the use of probe molecules to "report" on conditions in the hydrogenation reactor (10,11). Probe molecules serve the general function of sensing the reaction environment throughout the course of the liquefaction experiment. The information gained relates to the way the reaction environment is changed by the addition of components normally used in liquefaction such as coal, catalysts, and liquefaction solvents, or to changes in the process variables such as temperature, reaction time, or hydrogen pressure. Thus, the intent is not to ferret out the reaction mechanisms that are responsible for liquefaction, but to determine if a particular process variable selected for study may cause changes in the rates of certain types of reactions. Thus, a relatively stable compound, cis-decalin, was used to monitor the relative rates of free radical reactions as coal was added to the reaction system (11). It was shown that the presence of free radicals accelerates the isomerization of cis- to trans-decalin. The rate of approach to the equilibrium value for the ratio of cis- to trans-decalin was then used to evaluate the activity of the radicals generated in the liquefaction reactor. The addition of coal accelerated the rate of approach to equilibrium, thus indicating that coal acts as a free-radical reaction initiator. Further, the rate of approach to the equilibrium ratio conformed reasonably well to pseudo-first order rate behavior in the presence of coal, indicating that the activity of free radicals remained constant over the course of the reaction which lasted in this case up to three hours.

Other probes serve other purposes. For example, 1,3-dimethylnaphthalene, as described in the accompanying (12) and a prior paper (11), has been used to probe dealkylation reactivity. This probe revealed that the addition of coal increased the yield of

dealkylated products, indicating that coal may initiate hydrogen atom transfer reactions resulting in alkyl-aromatic bond cleavage, especially under hydrogen gas pressure. Cleavage of such bonds results from the transfer of hydrogen atoms from a donor or by the attachment of a free hydrogen atom. Each source of hydrogen has a different selectivity for attack at the 1- versus the 2-position on naphthalene. Significantly, the preference for cracking at the 1-position increases with addition of coal. Transfer of hydrogen atoms from hydroaromatic free radicals is known to be more selective for the 1-position than attack of the free hydrogen atom itself (5). Thus, the increase in selectivity indicates that a portion of the cracking reactions result from hydrogen atom transfer from active donors of the coal or coal-derived materials rather than the free hydrogen atom. This portion of the cracking reactions takes place primarily as a result of the direct interaction of the probe with added coal, and thus reflects the reactivity of the coal-derived hydrogen transfer agents.

Another approach to the problem of hydrogen transfer chemistry has been recently taken up. The coal-hydrogen-catalyst interaction is of fundamental importance to liquefaction schemes, and particularly those that focus on low severity processing conditions. In this connection, one of the major puzzles of liquefaction chemistry is how hydrogen transfer takes place between a solid, heterogeneous catalyst and a solid or nearly solid substrate like coal. A pulse-flow microreactor was constructed and demonstrated to be a useful means to study this chemistry (13). As shown in Figure 2, the reactor is a simple device designed to allow a sample to be heated in a tube placed in a clam-shell furnace. A stream of argon is passed through the tube and sampled by a quadrupole mass spectrometer that is capable of monitoring up to five different masses at once. An injection loop allows the introduction of a pulse of deuterium gas upstream of the heated sample. Using this apparatus, a series of samples was heated in separate experiments to determine if useful information could be obtained regarding the interaction of a solid, dispersed catalyst with coal in the absence of any liquefaction solvent. The first experiment indicates that some exchange takes place when a coal is heated by itself. As shown in Figure 3, passage of deuterium over coal heated to $425^{0}C$ results in the formation of small peaks for HD and H_2. The major peak due to D_2 itself remains. Thus, deuterium does exchange with hydrogen on coal in the absence of added catalyst. The next experiment involved heating MoS_3 by itself. This material has been used as a catalyst precursor by others at our laboratory with good results (14). As shown in Figure 4, when MoS_3 is heated to $400^{0}C$, the pulse of deuterium results in a family of pulses at m/e of 32, 33, and 34. A peak at 36 is also associated with this trio, but not shown in this figure. This family of peaks is due to D_2S and H_2S and their ionic fragments, and indicates that, under reducing conditions, hydrogen sulfide is evolved from the catalyst. Presumably, the hydrogen contained in the sulfides detected has come from exchange between water and D_2S at some point downstream from the catalyst bed. Significantly, no HD or H_2 is observed. Under these conditions, the catalyst is probably not yet fully reduced, and the evolution of hydrogen sulfide may reflect

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continuation of the transition from MoS_3 to MoS_2. Post-run characterization of the recovered catalyst may determine the final form of the material reached by the conclusion of the experiment.

The third experiment combined coal and catalyst. A mixture of the MoS_3 catalyst precursor and a Pittsburgh No. 8 coal from the Argonne Coal Sample Bank was heated, and its behavior was found to be much different than either material alone. (By itself, the Pittsburgh No. 8 coal responded very much like the Illinois No. 6 coal used in the initial experiment.) At 375^0C, the pulse of deuterium was not detected, implying that it was taken up by the coal/catalyst mixture. This behavior was not seen when either coal or this catalyst was used separately. At a higher temperature (Figure 5) the deuterium pulse is still missing, but a pulse of H_2 with roughly the same magnitude appeared. After cooling to room temperature, the sample was put through the same heating cycle once more. This time, hydrogen-deuterium exchange reactions were noted when the temperature reached 225^0C, far below that required on initial heat-up. This may reasonably be interpreted on the basis that the catalyst precursor, once activated by heating at a higher temperature, may now show activity at a much lower temperature. Again, the pulse of deuterium, when admitted at temperatures above 250^0C, was completely removed and a pulse of H_2 in the same shape appeared in its place. At present, the mechanism for this exchange process is not understood. However, it points out in a dramatic fashion that a "dry" system does exhibit chemical communication between coal and dispersed catalyst. These experiments are still in their infancy. The positive results in hand provide good reason to suspect that more can be learned about this fascinating transfer of hydrogen between coal, catalyst, and gas-phase hydrogen.

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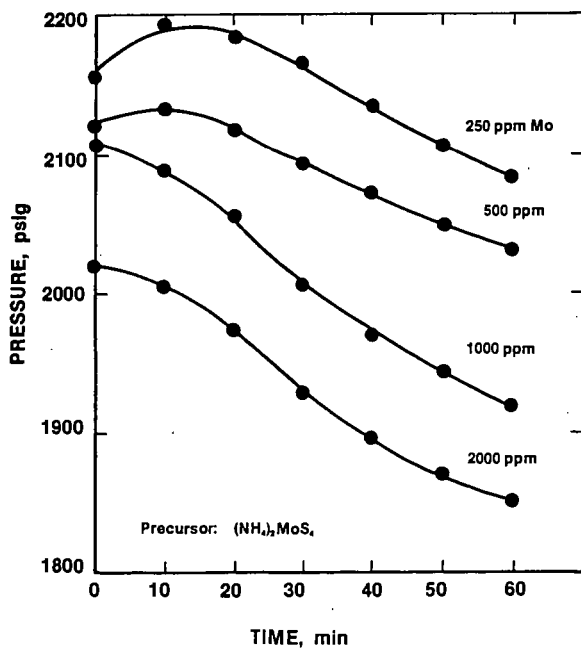   Div. Fuel Chem. Preprints, 34(4), 1423 (1989).

FIGURE 1.   TOTAL PRESSURE VERSUS TIME FOR LIQUEFACTION OF
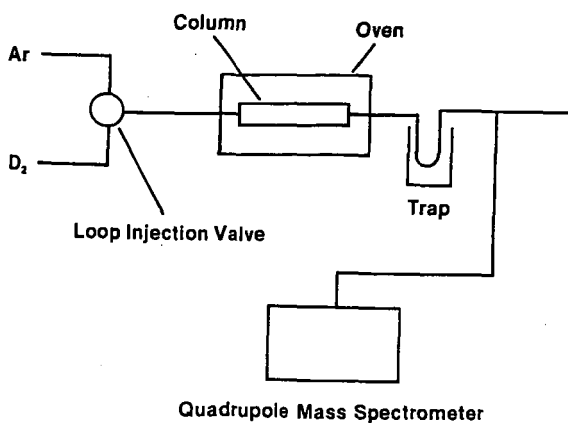   ILLINOIS No. 6 COAL AT 350°C.

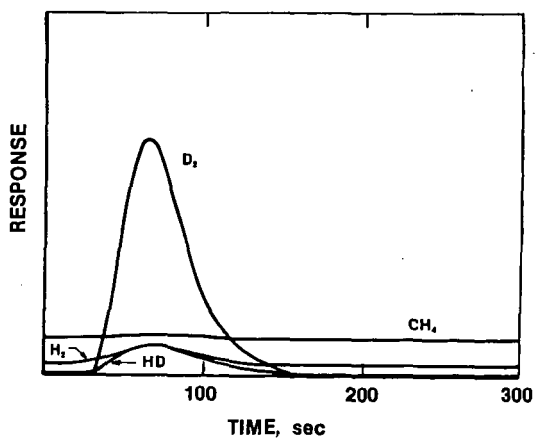FIGURE 2. PULSE-FLOW MICROREACTOR FOR MONITORING DEUTERIUM EXCHANGE.

FIGURE 3. EXCHANGE EXPERIMENT WITH DEUTERIUM PULSE AND ILLINOIS No.6 COAL HEATED AT 400°C.

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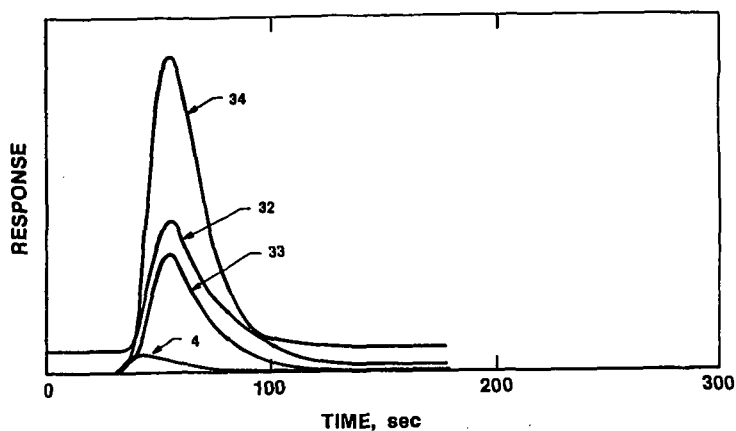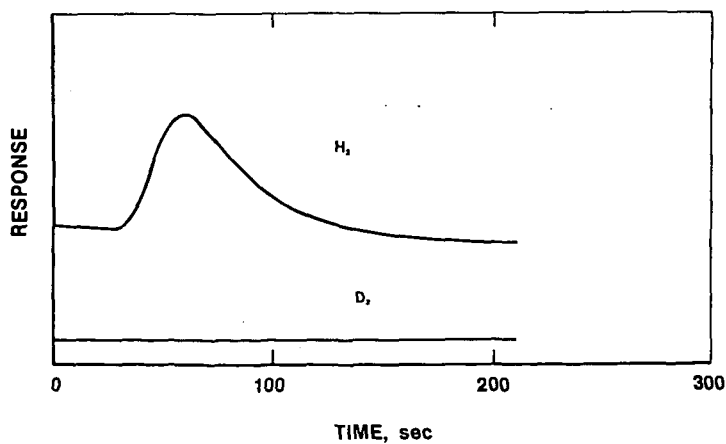FIGURE 4. RESPONSE FROM DEUTERIUM PULSE AFTER MoS$_3$ WAS HEATED TO 400^{0}C.

FIGURE 5. RESPONSE FROM DEUTERIUM PULSE AFTER A MIXTURE OF PITTSBURGH No. 8 COAL (1.9 g) AND MoS$_3$ (0.1 g) WAS HEATED TO 425^{0}C.